

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 January 2004 (29.01.2004)

PCT

(10) International Publication Number
WO 2004/009739 A2

- (51) International Patent Classification⁷: C10G 73/44, 45/58
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (21) International Application Number: PCT/EP2003/007785
- (22) International Filing Date: 17 July 2003 (17.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 02077921.1 18 July 2002 (18.07.2002) EP
- (71) Applicant (*for all designated States except US*): SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): HOEK, Arend [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL).
- (74) Agent: SHELL INTERNATIONAL B.V.; Intellectual Property Services, P.O. Box 384, NL-2501 CJ The Hague (NL).
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/009739 A2

- (54) Title: PROCESS TO PREPARE A MICROCRYSTALLINE WAX AND A MIDDLE DISTILLATE FUEL

(57) **Abstract:** Process to prepare a microcrystalline wax and a middle distillate fuel by (a) hydrocracking/hydroisomerising a Fischer-Tropsch product, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms, (b) performing one or more distillate separations on the effluent of step (a) to obtain a middle distillate fuel fraction and a microcrystalline wax having an initial boiling point of between 500 and 600 °C.

- 1 -

PROCESS TO PREPARE A MICROCRYSTALLINE WAX AND A MIDDLE DISTILLATE FUEL

The invention is directed to a process to prepare a Fischer-Tropsch derived microcrystalline wax.

A process route is disclosed for the preparation of Fischer-Tropsch derived microcrystalline wax products by the so-called Shell Middle Distillate Synthesis (SMDS) process is described in "The Markets for Shell Middle Distillate Synthesis Products", Presentation of Peter J.A. Tijm, Shell International Gas Ltd., Alternative Energy '95, Vancouver, Canada, May 2-4, 1995. This publication describes the preparation of various grades of wax products having congealing points ranging from 31 to 99 °C. The disclosed process involves a Fischer-Tropsch synthesis step wherein a waxy product is obtained. This product is first hydrogenated and the hydrogenated product is separated by means of distillation into the various wax product grades. The product with the highest congealing point is referred to as SX100.

Said presentation also discloses a process to prepare middle distillates by hydrocracking/hydroisomerisation of the Fischer-Tropsch synthesis product.

A disadvantage of the SX100 grade or similar commercial Fischer-Tropsch derived grades having a congealing point as determined by ASTM D 938 of between 85 and 120 °C is that they are too hard to be used in some applications. The hardness of a wax may be measured by the IP 376 method. Typical PEN values at 43 °C as obtained using this method on commercially available Fischer-Tropsch derived SX100 waxes are between 0.2 and 0.6 mm.

- 2 -

An almost similar process as the SMDS process disclosed in said presentation is disclosed in the recently published WO-A-0174969. In the disclosed process a Fischer-Tropsch product is subjected to a hydro-processing step at low conversion. The waxy products as obtained in the examples of said publication are characterized by means of a Needle Penetration Value according to ASTM D-1321. Because the temperature at which said value is measured is not provided no assessment of the softness of these products can be made. Furthermore a melting point is mentioned without providing a method on how this property was measured.

A disadvantage of the disclosed process in WO-A-0174969 or the disclosed SMDS process line-up is that a dedicated wax hydroconversion step is needed to prepare the wax products next to a dedicated middle distillate hydroconversion step to prepare middle distillates from a Fischer-Tropsch synthesis product.

The object of the present invention is to integrate the process of preparing soft waxes having a high congealing point with the production of middle distillate fuels having good cold flow properties.

The following process achieves this object. Process to prepare a microcrystalline wax and a middle distillate fuel by

(a) hydrocracking/hydroisomerising a Fischer-Tropsch product, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,

(b) performing one or more distillate separations on the effluent of step (a) to obtain a middle distillate fuel

- 3 -

fraction and a microcrystalline wax having an initial boiling point of between 500 and 600 °C.

Applicants found that by performing the hydro-cracking/hydroisomerisation step with the relatively heavy feedstock a process is obtained wherein in one hydrocracking step both middle distillates and a microcrystalline wax are obtained in a high yield. A further advantage of said process is that the fraction obtained boiling between said middle distillates and the microcrystalline wax is very suited as a lubricating base oil precursor. By dewaxing said fraction excellent quality base oils may be obtained.

The process of the present invention results in middle distillates having exceptionally good cold flow properties. These excellent cold flow properties could perhaps be explained by the relatively high ratio iso/normal and especially the relatively high amount of di- and/or trimethyl compounds. Nevertheless, the cetane number of the diesel fraction is more than excellent at values far exceeding 60, often values of 70 or more are obtained. In addition, the sulphur content is extremely low, always less than 50 ppmw, usually less than 5 ppmw and in most case the sulphur content is zero. Further, the density of especially the diesel fraction is less than 800 kg/m³, in most cases a density is observed between 765 and 790 kg/m³, usually around 780 kg/m³ (the viscosity at 100 °C for such a sample being about 3.0 cSt). Aromatic compounds are virtually absent, i.e. less than 50 ppmw, resulting in very low particulate emissions. The polycyclic aromatic content is even much lower than the aromatic content, usually less than 1 ppmw. T95, in combination with the above properties, is below 380 °C, often below 350 °C.

The process as described above results in middle distillates having extremely good cold flow properties.

For instance, the cloud point of any diesel fraction is usually below -18 °C, often even lower than -24 °C. The CFPP is usually below -20 °C, often -28 °C or lower. The pour point is usually below -18 °C, often below -24 °C.

5 The relatively heavy Fischer-Tropsch product used in step (a) has at least 30 wt%, preferably at least 50 wt%, and more preferably at least 55 wt% of compounds having at least 30 carbon atoms. Furthermore the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms of the Fischer-Tropsch product is at least 0.2, preferably at least 0.4 and more preferably at least 0.55. Preferably the Fischer-Tropsch product comprises a C₂₀₊ fraction having an ASF-alpha value (Anderson-Schulz-Flory chain growth factor) of at least 0.925, preferably at least 0.935, more preferably at least 0.945, even more preferably at least 0.955.

10 The initial boiling point of the Fischer-Tropsch product may range up to 400 °C, but is preferably below 200 °C. Preferably any compounds having 4 or less carbon atoms and any compounds having a boiling point in that range are separated from a Fischer-Tropsch synthesis product before the Fischer-Tropsch synthesis product is used in step (a). In addition to the Fischer-Tropsch product also other fractions may be additionally processed in step (a). Possible other fractions may suitably be any excess microcrystalline wax as obtained in step (b) or off-spec base oil fractions if base oils are also prepared in said process.

15 Such a Fischer-Tropsch product can be obtained by any process, which yields a relatively heavy Fischer-Tropsch product. Not all Fischer-Tropsch processes yield such a heavy product. An example of a suitable Fischer-Tropsch process is described in WO-A-9934917 and in AU-A-698392.

- 5 -

These processes may yield a Fischer-Tropsch product as described above.

The Fischer-Tropsch product will contain no or very little sulphur and nitrogen containing compounds. This is typical for a product derived from a Fischer-Tropsch reaction, which uses synthesis gas containing almost no impurities. Sulphur and nitrogen levels will generally be below the detection limits, which are currently 5 ppm for sulphur and 1 ppm for nitrogen.

The Fischer-Tropsch product may optionally be subjected to a mild hydrotreatment step in order to remove any oxygenates and saturate any olefinic compounds present in the reaction product of the Fischer-Tropsch reaction. Such a hydrotreatment is described in EP-B-668342. The mildness of the hydrotreating step is preferably expressed in that the degree of conversion in this step is less than 20 wt% and more preferably less than 10 wt%. The conversion is here defined as the weight percentage of the feed boiling above 370 °C, which reacts to a fraction boiling below 370 °C. After such a mild hydrotreatment lower boiling compounds, having four or less carbon atoms and other compounds boiling in that range, will preferably be removed from the effluent before it is used in step (a).

The hydrocracking/hydroisomerisation reaction of step (a) is preferably performed in the presence of hydrogen and a catalyst, which catalyst can be chosen from those known to one skilled in the art as being suitable for this reaction. Catalysts for use in step (a) typically comprise an acidic functionality and a hydrogenation/dehydrogenation functionality. Preferred acidic functionality's are refractory metal oxide carriers. Suitable carrier materials include silica, alumina, silica-alumina, zirconia, titania and mixtures thereof. Preferred carrier materials for inclusion in the

catalyst for use in the process of this invention are silica, alumina and silica-alumina. A particularly preferred catalyst comprises platinum supported on a silica-alumina carrier. If desired, applying a halogen moiety, in particular fluorine, or a phosphorous moiety to the carrier, may enhance the acidity of the catalyst carrier. Examples of suitable hydrocracking/hydro-isomerisation processes and suitable catalysts are described in WO-A-0014179, EP-A-532118, EP-A-666894 and the earlier referred to EP-A-776959.

Preferred hydrogenation/dehydrogenation functionality's are Group VIII noble metals, for example palladium and more preferably platinum. The catalyst may comprise the hydrogenation/dehydrogenation active component in an amount of from 0.005 to 5 parts by weight, preferably from 0.02 to 2 parts by weight, per 100 parts by weight of carrier material. A particularly preferred catalyst for use in the hydroconversion stage comprises platinum in an amount in the range of from 0.05 to 2 parts by weight, more preferably from 0.1 to 1 parts by weight, per 100 parts by weight of carrier material. The catalyst may also comprise a binder to enhance the strength of the catalyst. The binder can be non-acidic. Examples are clays and other binders known to one skilled in the art.

In step (a) the feed is contacted with hydrogen in the presence of the catalyst at elevated temperature and pressure. The temperatures typically will be in the range of from 175 to 380 °C, preferably higher than 250 °C and more preferably from 300 to 370 °C. The pressure will typically be in the range of from 10 to 250 bar and preferably between 20 and 80 bar. Hydrogen may be supplied at a gas hourly space velocity of from 100 to 10000 Nl/l/hr, preferably from 500 to 5000 Nl/l/hr. The hydrocarbon feed may be provided at a weight hourly space

velocity of from 0.1 to 5 kg/l/hr, preferably higher than 0.5 kg/l/hr and more preferably lower than 2 kg/l/hr. The ratio of hydrogen to hydrocarbon feed may range from 100 to 5000 Nl/kg and is preferably from 250 to 2500 Nl/kg.

5 The conversion in step (a) as defined as the weight percentage of the feed boiling above 370 °C which reacts per pass to a fraction boiling below 370 °C, is at least 20 wt%, preferably at least 25 wt%, but preferably not more than 80 wt%, more preferably not more than 70 wt%.

10 The feed as used above in the definition is the total hydrocarbon feed fed to step (a), thus also any optional recycle to step (a).

15 In step (b) one or more distillate separations are performed on the effluent of step (a) to obtain at least one middle distillate fuel fraction and a micro-crystalline wax having an initial boiling point of between 500 and 600 °C. Suitably more middle distillate fuel fractions are recovered from the effluent of step (a). Preferably at least two of the possible naphtha, kerosene or gas oil fractions are recovered from the product of step (a). Most preferably a gas oil fraction is isolated having the above described cold flow properties. This distillate separation is preferably performed by means of a distillation at about atmospheric conditions, preferably at a pressure of between 1.2-2 bara. The microcrystalline wax is preferably isolated from the bottom product as obtained in the atmospheric distillation by means of a distillation performed at near vacuum conditions. This atmospheric bottom product preferably boils for at least 95 wt% above 370 °C. The vacuum distillation is suitably performed at a pressure of between 0.001 and 0.1 bara. The wax is preferably obtained as the bottom product of such a distillation. The distillate fractions as obtained in such a distillation may be recycled to step (a) or used to

- 8 -

prepare lubricating base oils. This fraction may be further processed on site or sold as a waxy raffinate product. This product can be transported by for example ship or trains to base oil production facilities
5 elsewhere. This (base oil precursor) fraction as obtained in said vacuum distillation preferably has a T10 wt% boiling point of between 200 and 450 °C and a T90 wt% boiling point of between 300, and preferably between 400 and 550 °C.

10 The vacuum distillation of step (b) is preferably operated such that the desired congealing point of the microcrystalline wax is obtained.

15 The soft microcrystalline wax as obtained with the above process has preferably a congealing point as determined by ASTM D 938 of between 85 and 120 and more preferably between 95 and 120 °C and a PEN at 43 °C as determined by IP 376 of more than 0.8 mm and preferably more than 1 mm. The wax is further characterized in that it preferably comprises less than 1 wt% aromatic
20 compounds and less than 10 wt% naphthenic compounds, more preferably less than 5 wt% naphthenic compounds. The mol percentage of branched paraffins in the wax is preferably above 33 and more preferably above 45 and below 80 mol% as determined by C13 NMR. This method determines an
25 average molecular weight for the wax and subsequently determines the mol percentage of molecules having a methyl branch, the mol percentage of molecules having an ethyl branch, the mol percentage of molecules having a C3 branch and the mol percentage having a C4+ branch, under
30 the assumption that each molecule does not have more than one branch. The mol% of branched paraffins is the total of these individual percentages. This method calculated the mol% in the wax of an average molecule having only one branch. In reality paraffin molecules having more
35 than one branch may be present. Thus the content of

- 9 -

branched paraffins determined by different method may result in a different value.

The oil content as determined by ASTM D 721 is typically below 10 wt% and more preferably below 6 wt%.
5 If lower oil contents are desired it may be advantageous to perform an additional de-oiling step. De-oiling processes are well known and are for example described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, pages 162-165.
10 After de-oiling the wax preferably has a oil content of between 0.1 and 2 wt%. The lower limit is not critical. Values of above 0.5 wt% may be expected, but lower values can be achieved depending on the method in which the wax is obtained. Most likely the oil content will be between
15 1 and 2 wt%. The kinematic viscosity at 150 °C of the wax is preferably higher than 8 cSt and more preferably higher than 12 and lower than 18 cSt.

The invention will be illustrated with the following non-limiting examples.

20 Example 1

The C₅-C₇₅₀ °C+ fraction of the Fischer-Tropsch product, as obtained in Example VII using the catalyst of Example III of WO-A-9934917 was continuously fed to a hydrocracking step (step (a)). The feed contained about 25 60 wt% C₃₀+ product. The ratio C₆₀+/C₃₀+ was about 0.55. In the hydrocracking step the fraction was contacted with a hydrocracking catalyst of Example 1 of EP-A-532118.

The effluent of step (a) was continuously distilled to give lights, fuels and a residue "R" boiling from 30 370 °C and above. The yield of gas oil fraction on fresh feed to hydrocracking step was 43 wt%. The properties of the gas oil as obtained are presented in Table 1. The main part of the residue "R" was recycled to step (a) and a remaining part was separated by means of a vacuum distillation into a microcrystalline wax having the
35

- 10 -

properties as listed in Table 2. The fraction of microcrystalline wax obtained relative to the feed to the vacuum distillation was 63.2 wt%.

The conditions in the hydrocracking step (a) were: a
5 fresh feed Weight Hourly Space Velocity (WHSV) of 1.02 kg/l.h, recycle feed WHSV of 0.31 kg/l.h, hydrogen gas rate = 1000 Nl/kg, total pressure = 40 bar, and a reactor temperature of 329 °C.

Table 1

Gas oil properties	
Cloud Point	-20
CFPP	-21
Pour Point	<-24
Normals (wt%)	21.3
Iso's (wt%)	78.7
Mono-methyl	39.5
Di-methyl	25.5
Others	13.8
Density (kg/l)	0.78
Cetane (D976m)	77
Cetane (D4737m)	85
T95	360

Table 2

	SX100*	Parafin H1**	Product of Example 1
Congealing point (ASTM D-938; °C)	97.3	100	99
Drop melting point (ASTM D 127) (°C)	110.0	113.5	112.3
PEN at 25 °C (IP 376) (mm)	0.1	0.1	11.4
PEN at 43 °C	0.4	0.4	17.6
PEN at 65 °C	1.1	1.7	>20
Oil content (ASTM D 721; wt%)	< 0.1	Not measured	4.6
Kinematic viscosity at 150 °C (ASTM D 445)	7.97	Not measured	13.9
Micro-crystalline structure by microscopic observation	Yes	Yes	Yes

* SX100 is a Fischer-Tropsch wax as marketed by Shell Malaysia bhp

** Parafin H1 is a Fischer-Tropsch derived wax marketed by Schumann Sasol

C L A I M S

1. Process to prepare a microcrystalline wax and a middle distillate fuel by
 - (a) hydrocracking/hydroisomerising a Fischer-Tropsch product, wherein weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.2 and wherein at least 30 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms,
 - 10 (b) performing one or more distillate separations on the effluent of step (a) to obtain a middle distillate fuel fraction and a microcrystalline wax having an initial boiling point of between 500 and 600 °C.
2. Process according to claim 1, wherein at least 50 wt% of compounds in the Fischer-Tropsch product have at least 30 carbon atoms.
- 15 3. Process according to any one of claims 1-2, wherein the weight ratio of compounds having at least 60 or more carbon atoms and compounds having at least 30 carbon atoms in the Fischer-Tropsch product is at least 0.4.
- 20 4. Process according to any one of claims 1-3, wherein the conversion in step (a) is between 25 and 70 wt%.
5. Process according to any one of the claims 1-4, wherein the microcrystalline wax as obtained has a congealing point of between 95-120 °C and a PEN at 43 °C as determined by IP 376 of more than 0.8 mm.
- 25 6. Process according to claim 5, wherein the PEN at 43 °C is more than 1.0 mm.
7. Process according to any one of claims 1-6, wherein the wax obtained in step (b) is subjected to an

- 13 -

additional de-oiling step to obtain a wax having an oil content of between 0.1 and 2 wt%.

8. Microcrystalline wax having a congealing point of between 95 and 120 °C and a PEN at 43 °C as determined by IP 376 of more than 0.8 mm.

5